

Argonne National Laboratory

ENGINEERING DEVELOPMENT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 15. Material Balance Demonstrations,
Production Rates, and Fluorine Utilizations
in Fluorination of Kilogram Quantities
of PuF_4 to PuF_6 with Elemental Fluorine
in a Fluid-bed Reactor

by

N. M. Levitz, G. J. Vogel, E. L. Carls,
D. E. Grosvenor, W. F. Murphy,
B. J. Kullen, and D. J. Raue

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Chemical Engineering Division

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I. SUMMARY

A total of 2.3 kg of PuF_4 was fluorinated with elemental fluorine in a fluidized bed of alumina to provide information pertinent to fluoride-volatility process flowsheets. Fluorination rates above 6 lb/(hr)(sq ft) of PuF_6 and material balances near 100% were achieved.

The fluorination runs were divided into three campaigns, each campaign consisting of three separate fluorinations (260 g of -325 mesh PuF_4 powder each), followed by a fluorination-cleanup step in which plutonium deposited in the lines and equipment was recovered. A single bed of alumina, about 6.5 kg of nominal 48-100 mesh, was used in each campaign. A 93% F_2 -7% N_2 gas mixture served as the fluidizing gas and reactant.

The fluorinator off-gas was passed through cold traps to collect the PuF_6 . Except for a bleed stream, the remaining gas was recycled to the fluorinator. Makeup fluorine was added to counteract the dilution effect of nitrogen added as instrument purges and as blowback gas for the fluorinator filters. The temperature of the fluidized alumina bed was increased incrementally (about 25°C every 15 min) to 550°C from the initial temperatures of 300°C (Campaign 1), 375°C (Campaign 2), and 450°C (Campaign 3). Previous work had shown that lower initial temperatures decreased plutonium retention in the alumina bed. The total fluorination time for each run was 5 hr in the first and second campaigns and 3 hr in the third campaign.

The significant results from the campaigns are as follows:

1. Plutonium material balances were 97, 101, and 99%, values that are within the expected range.
2. Production rates of PuF_6 averaged 2.4 lb/(hr)(sq ft) for the first and second campaigns and 4.1 for the third campaign. Rates above 6 lb/(hr)(sq ft) were achieved in the beginning 30-min fluorination period.

3. Fluorine utilization efficiencies (defined as the amount of fluorine reacted to that which could theoretically react based on equilibrium considerations) averaged 22, 17, and 28% for the successive campaigns. Demonstrated efficiencies near 100% were attained in the earlier portions of a run when large quantities of plutonium were present.

4. Less than 2% of the PuF_6 was decomposed to PuF_4 by radiation decomposition, and this was refluorinated and recovered without difficulty.

Other information developed from the data shows the following:

1. As found earlier, the concentrations of plutonium in the samples removed from the fluidized alumina bed in the fluorinator do not reflect accurately the inventory of plutonium in the bed. Careful consideration must be given to fluid-bed systems of widely differing particle sizes, in terms of bed mixing and the problem of elutriation, in order to sample the bed effectively. In the present work, with PuF_4 of -325 mesh size nominal and 48-100 mesh alumina as bed materials, grab samples did not accurately reflect the inventory of the system, and the data could not be used to calculate PuF_6 production rates and fluorine efficiencies.

2. The cold traps for collecting PuF_6 from the process-gas stream operated efficiently with -65°C coolant. The two in-series cold traps removed 98.7% of the PuF_6 passing through them, which is near the theoretical amount that could be removed as determined from extrapolated vapor-pressure data.

3. Corrosion of the fluorinator is not a problem under our operating conditions. The corrosion rate, based on continuous operation for a 24-hr day, 365-day year, was less than 30 mils/yr.

4. Development of neutron-counting techniques for monitoring (1) the movement of PuF_4 and PuF_6 during fluorination of PuF_4 in fluid beds and (2) the transfer of PuF_6 from one vessel to another shows promise. The end points of both the fluorination and the transfer operations in the current campaign were clearly indicated on the recorder traces.

5. A straight-line, log-log correlation was obtained when the neutron emission rate per gram of sample was plotted against the plutonium concentration obtained by analysis of NaF material on which PuF_6 has been sorbed. Similar correlations were not obtained for samples from the final alumina bed, the fluidized alumina bed, or the fluorinator wall and filter. The latter samples contained americium, like plutonium an alpha emitter that contributed to the $\text{F}(\alpha, n)\text{Na}$ reaction.

6. Sodium fluoride efficiently sorbed PuF_6 from the process-gas streams. Loadings of up to 25% plutonium were obtained.

7. The concentration of americium (from ^{241}Pu decay) in the fluorinator bed increased in succeeding fluorination runs of a campaign.

II. INTRODUCTION

Fluid-bed fluoride-volatility processes for the recovery of uranium and plutonium values from irradiated, low-enriched UO_2 elements clad in either Zircaloy or stainless steel have been under development at Argonne National Laboratory (ANL). General and specific papers describing the process and related experimental work have been published.^{1,2} Research and development work on volatility processes being done at ANL and other sites is reviewed quarterly in Reactor and Fuel Processing Technology (previously, Power Reactor Technology and Reactor Fuel Processing and Reactor Fuel Processing).

Two fluoride-volatility process flowsheets have been proposed. The first entails the following discrete steps:

1. Charging. Charging of the fuel assemblies to a fluid-bed reactor which contains a bed of alumina, the heat-transfer medium. The cladding encasing the oxide fuel pellets can be either Zircaloy or stainless steel.
2. Decladding. Removal of Zircaloy cladding by reaction of the zirconium with HCl to form volatile ZrCl_4 , while the unreacted UO_2 - PuO_2 pellets remain in the reactor bed. For stainless steel cladding, the cladding is disintegrated and the pellets are pulverized by HF-O_2 treatment at 550°C . Alternatively, either cladding could be removed mechanically.
3. Oxidation. Oxidation of the unreacted UO_2 - PuO_2 pellets from the Zircaloy decladding step to form U_3O_8 powder, which has a high surface area that increases the production rate in the subsequent fluorination steps.
4. Uranium Recovery. Separation of uranium from plutonium by reacting the uranium with BrF_5 to form volatile UF_6 , which leaves the reactor in the gas stream accompanied by bromine halides and volatile fission-product compounds that must be separated later.
5. Plutonium Recovery. Removal of plutonium from the reactor by reacting it with fluorine to form volatile PuF_6 , which exits from the reactor in the gas stream, accompanied by a small amount of volatile fission-product compounds from which the PuF_6 must be subsequently separated.

In the second process flowsheet, the first and second steps (decladding and oxidation) are the same as in the first process flowsheet. In the third step, instead of preferential removal of uranium with BrF_5 , both uranium and plutonium are fluorinated simultaneously by using elemental fluorine. The resulting hexafluorides are separated from each other and from accompanying volatile fission-product fluorides by processes based on volatility, sorption, or selective chemical-reaction properties.

In both process flowsheets, the conditions for the fluorination of plutonium to PuF_6 , for the transport of PuF_6 through the system, and for

the collection of the PuF_6 are of particular interest. Also, since PuF_6 can be reduced to nonvolatile PuF_4 by alpha radiation and thermal-decomposition mechanisms and by reduction with compounds or metal surfaces of the equipment, the recovery of this PuF_4 from the equipment must be demonstrated.

Earlier investigations² using charges of 20-100 g of plutonium demonstrated that PuF_6 could be transported and collected readily and that plutonium deposited in equipment could be recovered using practical operating conditions. Fluorination data were obtained on: (1) $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ (fission product) pellets, (2) PuF_4 , and (3) plutonium remaining after $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets had been oxidized and the oxidized fines fluorinated with BrF_5 .

In the current investigation, designed to demonstrate that processing of plutonium by fluoride-volatility methods is practical, larger quantities of plutonium, 200 g of plutonium (about 260 g of PuF_4), were fluorinated and transferred from the fluorinator to other vessels in each run. Nine charges of PuF_4 were fluorinated totaling 2.3 kg (1.8 kg of plutonium). The fluorinations were divided into three campaigns, each campaign consisting of three fluorination runs followed by a plutonium cleanup run to remove plutonium deposited in the equipment. The campaigns differed in the starting fluorination temperature and the duration of fluorination. Primarily, these runs were made to demonstrate the following:

1. Good plutonium material balances can be achieved.
2. Practical production (fluorination) rates for PuF_6 from PuF_4 can be achieved.
3. Transport of PuF_6 through engineering-scale equipment presents no unusual problems.
4. Process losses of plutonium in the discarded alumina bed are acceptably low.
5. Plutonium deposited as a result of alpha radiation decomposition or because of interaction with the system (nickel equipment or other equipment constituents) can be recovered in the plutonium cleanup step.

III. EXPERIMENTAL PROCEDURE

A. Materials

Input materials included PuF_4 , alumina, and NaF . The PuF_4 was obtained as a fine powder, almost all less than -325 mesh, and relatively pure. Plutonium contents of two analyzed samples were 76.0 and 78.0%, an average of 77.0%, compared to 75.9% plutonium in PuF_4 . Isotopic contents on a weight-percentage basis were: ^{238}Pu , 0.06; ^{239}Pu , 85.91; ^{240}Pu , 11.40; ^{241}Pu , 2.38; ^{242}Pu , 0.25. Americium content was approximately 0.1%.

The alumina used as the heat-transfer medium in the fluorinator was Alcoa T-61 grade, nominal 48-100 mesh, and was used as received. A screen analysis is given in Table I. A single 6500-g bed of prefluorinated alumina was used in each campaign.

TABLE I. Particle Size Distribution, Alcoa T-61, Nominal 48-100 Mesh Alumina^a

US Sieve Size	w/o	US Sieve Size	w/o
+45	0.1	-120 +170	4.4
-45 +60	7.3	-170 +230	0.5
-60 +80	57.1	-230 +325	0.4
-80 +120	30.0	-325	0.2

^aSample sieved by placing screens on shaking tray for 15 min.

The pellets of NaF for sorbing PuF₆ were 1/8 in. high by 1/8 in. in diameter and were prepared by desorbing HF from NaF·HF pellets. Residual HF content was about 0.02%.

The activated alumina for sorbing or reacting fluorides and fluorine from process off-gas was Alcoa 8-14 mesh.

B. Equipment

The process equipment and engineering alpha facility have been described in earlier reports^{2,3} and will be described only briefly here. Two alpha containment boxes hold the process equipment. Control and monitoring equipment instruments are located on panels adjacent to the cell housing the large process-equipment alpha box.

The PuF₆ process equipment occupies one-half of the alpha box (as shown in Fig. 1). A schematic equipment flowsheet (Fig. 2) shows the fluorinator, its two primary filters (blowback filters), the secondary (or backup) filter outside the fluorinator, the two in-series cold traps for collecting hexafluoride product, and the recycle pump for recirculating the fluorine to the fluorinator. Since nitrogen is added to the circulating-gas loop as blowback gas and instrument purge gas, and fluorine is added to counter the dilution effect of the nitrogen, the pressure in the loop is maintained constant by bleeding a portion of the gas to the off-gas system. In this system, the bleed stream is passed first through NaF (3-in.-diam, 2½-ft-long trap), which efficiently sorbs the hexafluorides that have not been condensed in the cold traps, and second through activated alumina (4-in.-diam, 5-ft-long trap), which reacts with the fluorine. Inert gases then pass through a spray scrubber, three absolute filters, another spray scrubber, and another two absolute filters. Not shown in Figs. 1 and 2 are the NaF-filled traps used for final disposition of all the PuF₆ produced during the campaigns.

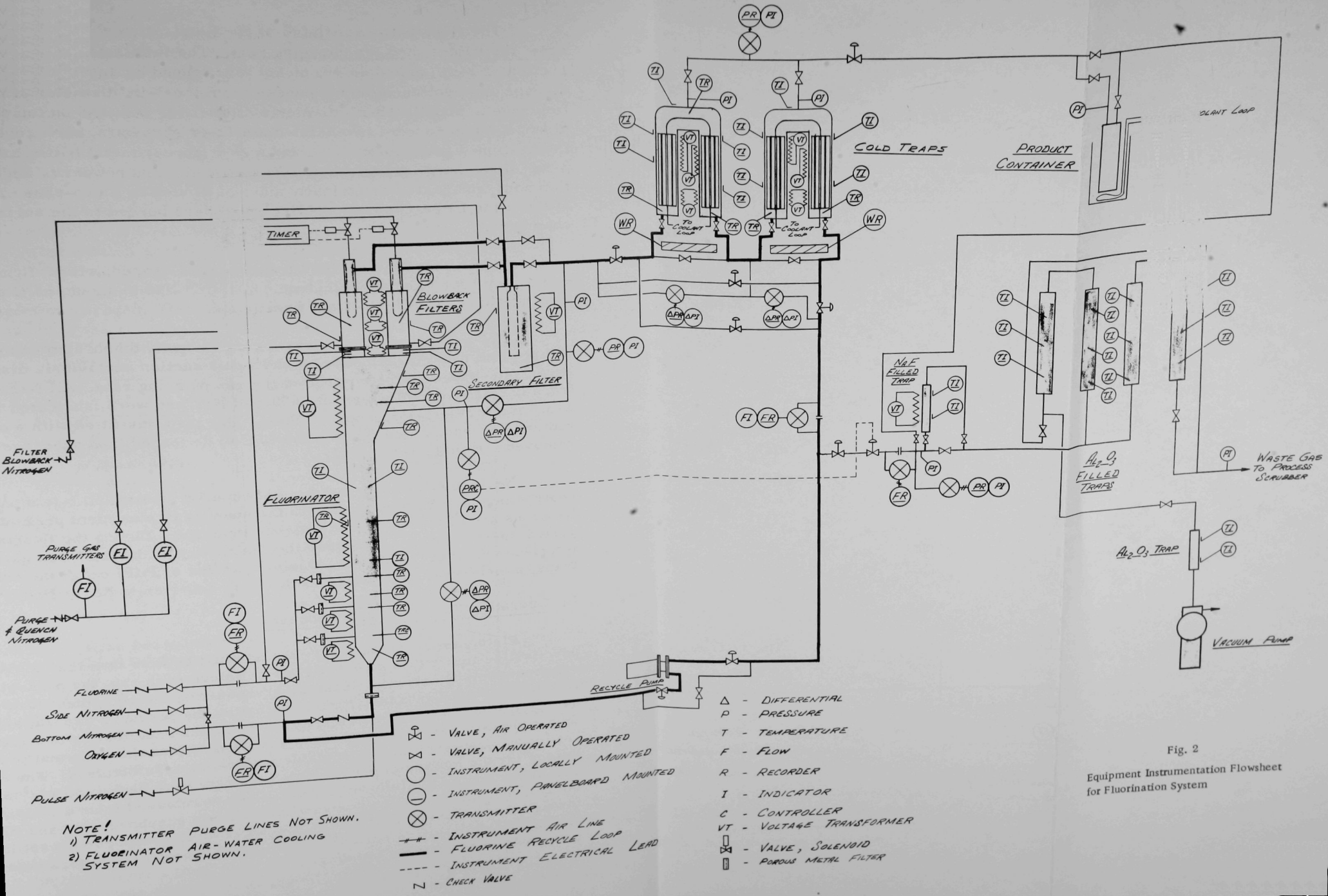


Fig. 2
 Equipment Instrumentation Flowsheet
 for Fluorination System

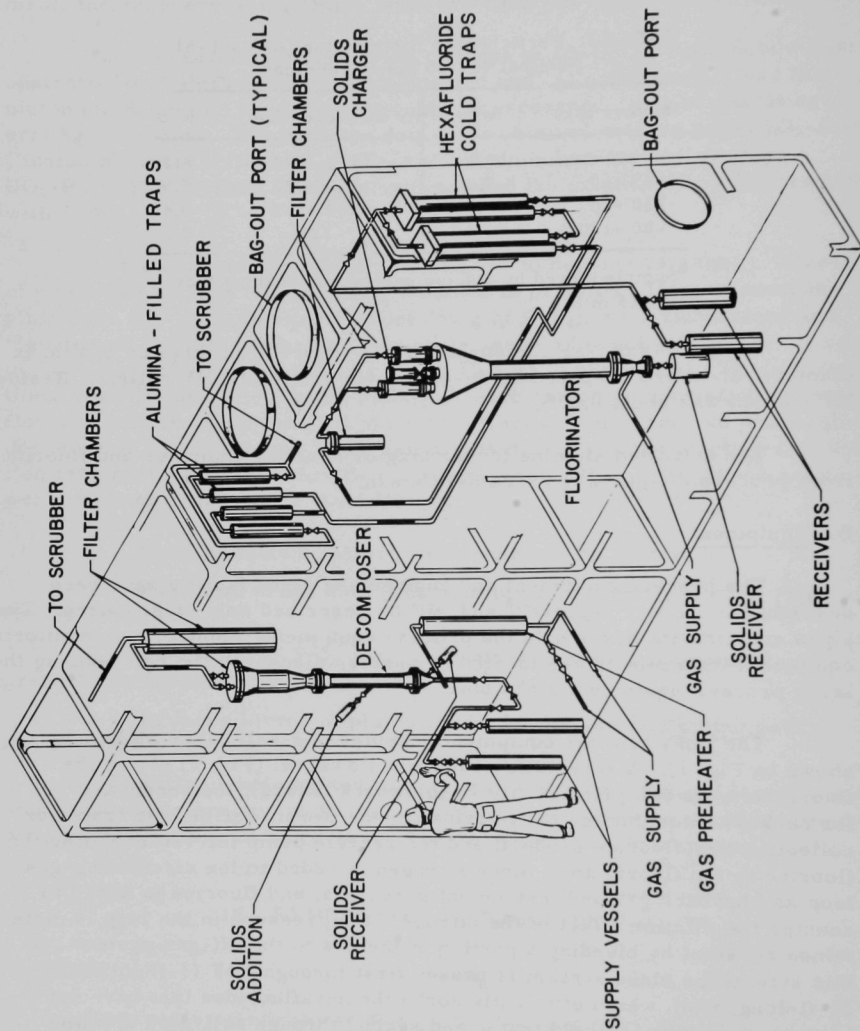


Fig. 1. Process Equipment in Glovebox

The fluorinator consisted of the fluidization zone, the disengaging zone, the filters, and the charging port. The fluidization zone was a 4-ft section of 3-in., Schedule 40, nickel pipe topped by an 18-in.-long conical disengaging section, which expanded from the 3-in. diameter at the fluidization zone to about a 15-in. diameter at the top. Mounted on top of the disengaging zone were two 4-in.-diam filter chambers, each containing an inside-finned gas-cooling zone and a 20- μ porous metal filter, and a 3-in.-diam charging port for the PuF_4 and alumina powders. The fluidization zone was heated electrically and was cooled by a two-phase air-water system; the filter-chamber cooling coils were bonded to the surface of the chambers.

The PuF_6 collection cold traps were U-shaped, with 3-ft legs of 4-in.-diam pipe. Trichlorethylene coolant chilled to about -65°C passed through a central 3/4-in.-diam finned pipe.

The gas-recycle pump was a remote-head, diaphragm compressor with a rated capacity of 2.0 scfm at 15 psia suction and 30 psia discharge. A variable-speed motor controlled the gas pumping rate. All NaF-filled traps normally contained about 2600 g of NaF and were fabricated from 3-in.-diam, 30-in.-long copper tubing. The trap was fitted with a central rod and screens, which allowed the NaF to be loaded (and subsequently removed for analysis) in layers.

Neutron count-rate meters were placed strategically to monitor neutron levels, which changed with the quantity of plutonium present. Neutrons are produced by the $\text{F}(\alpha, n)\text{Na}$ reaction. During the fluorination period, meters were placed near the fluorinator at the fluid-bed gas-solid interface and at the cold trap. During transfer of PuF_6 out of the cold traps, a meter was also placed at the PuF_6 receiver, a NaF-filled trap.

C. Operating Conditions and Procedure

Plutonium in the building exhaust must be less than the established permissible limits (3.2×10^{-11} $\mu\text{g}/\text{ml}$). Before each run, the pilot-plant equipment was checked for leaks by pressurizing the equipment to 15 psia, isolating the plant into four parts, and noting the pressure drop, if any, during a time interval (generally 1/2 hr). Leaks contributing to a higher than allowable leak rate were found and plugged, and the leak-test procedure was repeated until acceptable leak rates were obtained. The calculations for the maximum permissible leak rate have been reported² and assume or utilize the following: 100% PuF_6 is released from a leak into the box ventilation air; the box ventilation air is scrubbed once and filtered through three absolute filters; the box air is diluted with room-ventilation air; and this mixture is scrubbed and filtered through two filters before being exhausted from the building.

After the leak test, about 6.5 kg of alumina was added to the fluorinator and fluidization started with nitrogen. Heat was applied, and when 150°C was reached, 0.15 scfm of fluorine was added to the recycle-gas stream to prefluorinate the bed. Prefluorination was continued while the temperature of the bed was increased to 550°C over a 2-hr period, then held at 550°C for another 2-hr period. The fluidizing-gas velocity, with the bed at 550°C and a reactor pressure of 5 psig, was 0.73 ft/sec; the fluorine concentration was sustained at ~80%. This procedure was used for each campaign using a new alumina bed.

Three batches of about 260 g of PuF_4 each were processed in each campaign. After a batch of PuF_4 was charged to the alumina (and after final leak-testing of the charging flange seal), the bed was heated to the starting fluorination temperature of 300°C (first campaign only) while it was fluidized with 1.2 scfm of nitrogen. Gas recycle was initiated and 0.25 scfm of fluorine was added to the recycle loop to keep the fluorine concentration (at steady state) at 93%. For the three runs of the first campaign, the bed

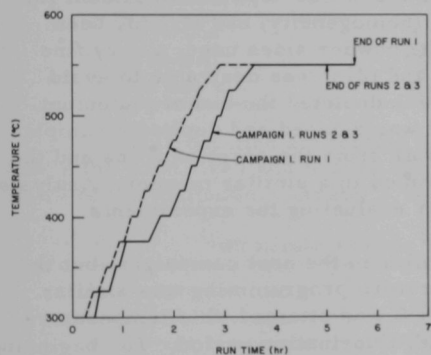


Fig. 3. Time-Bed-temperature Data for Fluorination Runs 1, 2, and 3 of the First Campaign

temperature was increased to 550°C (nominally, at 25°C/15 min, a rate selected from data obtained using neutron counts to follow the fluorination rate) and maintained there for 2 hr, as shown in Fig. 3. Additional time was taken in the first run (Pu-17) to reach 550°C as a result of the period at 375°C being extended to obtain neutron count-rate data. This run lasted 5.6 hr, the other two runs lasted 5 hr. The gas velocity in the reactor was allowed to increase with increasing temperature from 0.60 to 0.86 ft/sec.

When a PuF_4 batch fluorination was completed, the reactor heat

was turned off, fluorine flow stopped, and full nitrogen flow recycled through the bed until the bed temperature cooled to 300°C. Recycle flow was then stopped, and the nitrogen flow was reduced to 0.15 scfm. This nitrogen was routed through the cold traps (which had been kept at about -65°C) and then through a NaF-filled PuF_6 sorbent trap and a backup NaF trap. The temperature of the PuF_6 in the cold traps was gradually increased to ~70°C, effecting the inert-gas transfer of PuF_6 from the cold traps to the NaF.

The above procedure was repeated with a second and then a third 260-g charge of PuF_4 . Before the third transfer of PuF_6 from the cold traps to the NaF traps, a plutonium cleanup-fluorination of the primary fluorinator filters was completed. Particulate plutonium retained on the

filters was recovered by increasing the temperature in the filter zones to 300°C and maintaining this temperature for 2 hr while fluorine was recycled through the system; this PuF_6 was collected on a separate NaF trap placed in the exit line of the fluorinator. The bed in the fluorinator was kept at 550°C during this step. The PuF_6 was then transferred from the cold traps to NaF.

After this third transfer of PuF_6 from the cold trap to NaF, a plutonium-cleanup fluorination of the equipment was carried out. Any plutonium deposited on the surfaces of the secondary filter, the cold traps, and connecting lines by radiation decomposition of PuF_6 or reaction with the materials of construction was recovered by heating the equipment to 300°C and recycling 80% fluorine through the equipment for $2\frac{1}{2}$ hr. This PuF_6 also was sorbed on NaF in a separate trap.

The fluidized bed was sampled after each fluorination run, and again in the third fluorination run, after the filter cleanup step had been completed. Sampling of the fluidized alumina bed was kept to a minimum for two reasons: (1) Complete bed mixing (homogeneity) had already been shown to be questionable² because of the powder sizes used, a very fine PuF_4 and a relatively coarse alumina; and (2) it was desirable to avoid having to account for side streams, which depleted the bed of plutonium. After the third run, the fluorinator bed was dumped and duplicate samples were removed by using riffles. The NaF from the sorption traps and the activated alumina were ground and sampled in a similar manner. Analysis of the NaF served as the chief basis for evaluating the experiments.

Operating procedures were similar in the next campaigns, but the operating conditions were not. Temperature programming was similar, 25°C increments every 15 min until 550°C was attained, this temperature being held for the remainder of the PuF_4 fluorination period. The beginning fluorination temperature in each campaign was different--300, 375, and 450°C for Campaigns 1, 2, and 3, respectively--to determine if this affected the plutonium concentration in the bed at the end of the campaign. In the third campaign, the time for each PuF_4 fluorination was reduced from 5 hr of the earlier campaigns to 3 hr to determine the effect of reduced time on fluorine efficiency and production rate.

A minor procedural variation in the third campaign was that in the first two runs of this campaign the PuF_6 from the PuF_4 fluorination step was collected in one NaF trap for the first half-hour and in a second NaF trap for the second half-hour; during the rest of the fluorination step, the PuF_6 was collected in the cold traps from which it was transferred to NaF. At the end of the half-hour periods and at the end of each run, samples were removed from the fluidized bed. Besides providing production-rate data during the high rate periods at the start of a run, this procedure also allowed us to determine whether bed sample data could be used to calculate the PuF_6 production rate and fluorine efficiency.

IV. RESULTS AND DISCUSSION OF RESULTS

A. Plutonium Material Balance

Satisfactory plutonium material balances were obtained overall and in each of the three campaigns. The overall plutonium material balance was 99.0%; individual campaign balances were 97.1, 101.0, and 98.9%. Any value within the 96-104% range would have been considered satisfactory since it had been established earlier that, with our sample-preparation and analytical errors, the plutonium content at the 95% confidence level would be known to about ± 4 and $\pm 2\%$ for the output and input materials, respectively. Material-balance data for the three campaigns are summarized in Table II.

TABLE II. Summary of Plutonium Material-balance Data, All Campaigns

	Campaign			Total	All Campaigns (%)
	1	2	3		
Plutonium Charged, g	591.9	587.1	577.7	1756.7	100.0
Plutonium Recovered, g					
Plutonium Volatilized from Fluorinator	524.3	590.1	568.5	1682.9	95.8
Other Plutonium	50.3	2.6	3.0	55.9	3.2
Total Recovered	574.6	592.7	571.5	1738.8	
Plutonium Recovered, %	97.1	101.0	98.9	99.0	

A more detailed accounting of the plutonium is presented in Table III where the volatilized and nonvolatilized fractions have been listed. About 95.8% of the plutonium charged in all experiments was volatilized from

TABLE III. Details of Plutonium Material-balance Data, All Campaigns

	Campaign			Total Pu (g)	Pu (%)
	1 Pu (g)	2 Pu (g)	3 Pu (g)		
Charged	591.9	587.1	577.7	1756.7	100.0
Recovered					
Volatilized Plutonium:					
PuF ₆ transferred from cold traps to NaF or collected directly on NaF	492.1	574.0	527.4	1593.5	90.7
Recovered during filter fluorination step and collected on NaF	10.5	4.1	28.7	43.3	2.5
Recovered by fluorinating plutonium that had been deposited in the secondary filter and cold traps by radiation decomposition	8.6	8.0	7.6	24.2	1.4
Recovered from process off-gas stream by sorption on NaF during PuF ₄ fluorination step	13.1	4.0	4.8	21.9	1.2
Subtotal, Volatilized Plutonium	524.3	590.1	568.5	1682.9	95.8
Nonvolatilized Plutonium:					
Final bed	0.6	2.2	2.2	5.0	
Cleanout of fluorinator after campaign	-	0.4	0.8	1.2	
Filter cooling zone case	49.7	-	-	49.7	
Subtotal, Nonvolatilized Plutonium	50.3	2.6	3.0	55.9	3.2
Total Recovered	574.6	592.7	571.5	1738.8	99.0
Deficit or Excess	-17.3	+5.6	-6.2	-17.9	-1.0

the fluorinator. Nine-tenths of that not volatilized was contained in a cake found in the fluorinator filter chamber in the heat-exchange zone after the first campaign had been completed. If this cake formation is considered atypical (since this was the only one found in 28 fluorination runs) and the plutonium in the cake is disregarded, over 99% of the plutonium was volatilized from the fluorinator.

B. PuF_6 Production Rate

The average PuF_6 production rates for the successive campaigns were 2.4, 2.4, and 4.1 lb/(hr)(sq ft). The 70% higher rate in the third campaign resulted from reducing the 5-hr PuF_4 fluorination period to 3 hr. To determine the quantity of PuF_6 produced in a campaign, we assumed that all the PuF_4 charged was fluorinated to PuF_6 , except for that in the alumina bed at the end of the last run of each campaign. Actually, not all this plutonium was fluorinated, some being collected on the walls of the equipment, and, in one case, in a cake in the filter region. In making the calculations, we also assumed that all the plutonium was fluorinated in the 5- or 3-hr PuF_4 fluorination period and none in the plutonium-cleanup fluorination period of the equipment at the end of each campaign. Data are shown in Table IV.

TABLE IV. Operating Data and Results for All Campaigns

Campaign No.	Starting Fluorination Temperature (°C)	Run Duration (hr)	Plutonium in Fluorinator Bed at End of Campaign (%)	Percent of Charged Plutonium Volatilized from Bed	Average PuF_6 Production Rate [lb/(hr)(sq ft)]	Average Fluorine Efficiency (%)
1	300	5	0.010	99.9	2.4	22
2	375	5	0.029	99.7	2.4	17
3	450	3	0.022	99.8	4.1	28

A more exact method of determining the amount of PuF_6 produced--sorption of the PuF_6 on NaF and analysis of the NaF--was used to obtain production rates in successive time periods of the first and second runs of Campaign 3. The rate data (see Table V) for the first half-hour, second half-hour, and the rest of the run show that the rate is a direct function of the quantity of plutonium in the alumina bed. The slightly higher rate in the second run, as compared to the first run for the same time period, reflects the higher plutonium content of the alumina bed in the second run. The rates during the first half-hour period in each run were not the maximum that could be achieved even though the fluorine efficiency was near 100% (see Section C below). Higher rates could have been achieved if the fluorine concentration had been higher (the concentration was being increased from 0 to 93% at the start of the run) or if the throughput of fluorine had been increased. Higher starting temperatures than 450°C would also have increased the production rate. These results indicate that fluorination rates for plutonium, though substantially lower than for uranium, are adequate for practical applications.

TABLE V. PuF_6 Production Rates for Runs 1 and 2,
Campaign 3

Conditions:

Fluorine concentration in recycle gas started at 0% and increased to a maximum of ~92% in a half-hour period.

Fluorinator bed temperature started at 450°C, increased to 550°C during 1.25 hr and held at 550°C thereafter.

	Average PuF_6 Production Rate [lb/(hr)(sq ft)]	
	Run 1	Run 2
First half-hour	5.20	6.53
Second half-hour	4.70	6.41
Second and third hours	2.25	2.97
Entire run, average	3.15	4.13

C. Fluorine Efficiency

Fluorine efficiency is defined as the ratio of the quantity of PuF_6 produced by the $\text{PuF}_4\text{-F}_2$ reaction to the maximum quantity that could be produced as calculated from chemical equilibrium considerations, or

$$\text{Fluorine efficiency, \%} = 100 \times \frac{\text{gram-moles of } \text{PuF}_6 \text{ produced in a given time}}{K_{\text{eq}} \times \text{gram-moles of fluorine into fluorinator per given time}},$$

where

$$K_{\text{eq}} = \text{equilibrium constant for the reaction } \text{PuF}_4 + \text{F}_2 \rightleftharpoons \text{PuF}_6.$$

For total run efficiency calculations, as in the production-rate calculations described in Section B above, the amount of PuF_6 produced in a campaign was determined from the difference in the total quantity of plutonium charged in the three runs and the amount in the bed at the end of the third run. Calculated in this way, the fluorine efficiencies averaged 22, 17, and 28% for succeeding campaigns. The higher efficiency obtained in Campaign 3 was a direct result of decreasing the PuF_4 fluorination time from 5 to 3 hr; this change eliminated the low-efficiency end-of-run period.

Efficiencies for high-rate periods within a run were calculated for Runs 1 and 2 in Campaign 3 in which the PuF_6 was collected on separate NaF traps. In the first half-hour of Run 2, efficiencies near 100% were attained, as shown in Table VI. The plot of efficiency as a function of the amount of plutonium in the bed (Fig. 4) shows that the efficiency is high when the plutonium content of the fluorinator alumina bed is high and

becomes lower as the inventory of plutonium decreases. For a comparable period, the efficiency was higher in the second run than in the first because more plutonium was present in the fluorinator during the same time period. (Calculations show that only five-sixths of the plutonium charged in the first run was fluorinated. The remaining one-sixth was present at the start of the second run along with the fresh plutonium charge of the second run.) The data indicate that with about 200 g of plutonium in the fluorinator, efficiencies near 100% can be achieved even with low fluorine concentration and temperatures as low as 450°C.

TABLE VI. Fluorine Efficiencies during Different Time Periods of First and Second Runs of Campaign 3

Time Period	Operating Conditions in Period		Run 1			Run 2		
			Amount of Plutonium in Fluorinator (g)		Fluorine Efficiency (%)	Amount of Plutonium in Fluorinator (g)		Fluorine Efficiency (%)
	Fluorine Conc in Fluorinator	Fluid-bed Temp (°C)	Beginning of Period	End of Period		Beginning of Period	End of Period	
First half-hour	Increasing 6 → 91%	Increasing 450 → 525	194.3	145.1	77	228.0	180.0	98
Second half-hour	91 → 92½%	525 → 550	145.1	108.1	42	180.0	129.4	51
Final 2 hr	92½%	550	108.3	33.7	17	129.4	35.7	20

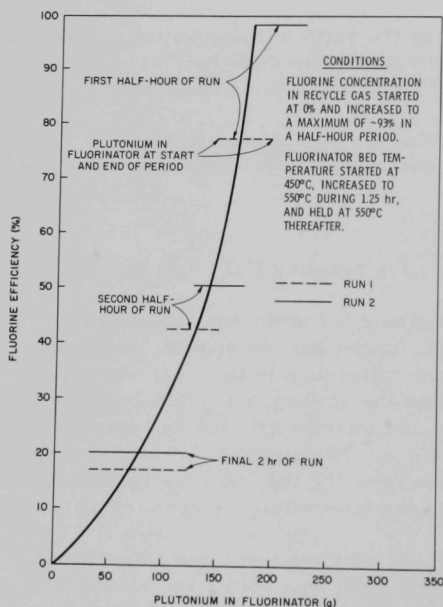


Fig. 4. Fluorine Efficiency as a Function of the Amount of Plutonium in Fluorinator, Runs 1 and 2, Campaign 3

D. Plutonium Loss in Discarded Alumina Bed from the Fluorinator

The quantity of nonvolatile fission products in the alumina bed of the fluorinator will increase in either batch or continuous processing of spent nuclear fuel elements; an exception would be the single use of an alumina bed per charge of fuel in the batch-processing case. Because heat is generated by decay of the fission products, the alumina bed, in total or in part, must be discarded and replaced. This discarded alumina is a process waste stream in which the plutonium concentration must be kept as low as possible to avoid the economic penalty of discarding valuable fissile material.

Material-balance data, in Table III, show that acceptably low plutonium concentrations have been achieved. The amounts of

plutonium in the beds at the end of the succeeding campaigns were 0.6, 2.2, and 2.2 g, or a total of 5 g for the three campaigns. This is, respectively, 0.1, 0.4, and 0.4% for the three campaigns, or a total loss of 0.3% of the plutonium charged. This is not a lower limit. More plutonium could probably have been removed from the bed if fluorination had been continued for a longer time.

E. Recovery of Plutonium Deposited in Equipment

Plutonium tetrafluoride can be deposited in equipment by different mechanisms--alpha-radiation decomposition of PuF_6 (in cold traps), thermal decomposition of PuF_6 (in the fluorinator filter chamber), elutriation from the bed during the fluorination (in the fluorinator), and reaction with the materials of construction. This PuF_4 is recovered by heating the equipment items to 300°C and recirculating fluorine through them.

Experimentally, the radiation decomposition rate has been found to be less than 2% per day.⁴ Although no rate could be determined from the data in Table III, a total of 24.2 g (1.4% of the plutonium charged) was recovered from the cold traps, the secondary filter, and off-gas lines between the fluorinator and the cold traps. Almost all the plutonium should have been deposited as a result of radiation decomposition. Although some PuF_6 may have reacted with metal surfaces, this source should be negligible since the equipment had been used to process over 500 g of PuF_6 . Some plutonium could have been present as PuF_4 dust that had passed through the pores of the filters in the fluorinator. Again, this amount should be negligible.

Data in Table III show also that 43.3 g (about $2\frac{1}{2}\%$ of the plutonium charged) was recovered during the filter-cleanup step when the temperature in the filter chambers was increased from 150 to 300°C while fluorine was circulated through the reactor. Not all of this necessarily came from the filter region since, while the filter region was being fluorinated, the alumina bed was kept at a fluorination temperature of 550°C and plutonium present here was also being fluorinated. The amount contributed by fluorination of the bed was probably small in the first and second campaigns since a total of only 10.5 and 4.1 g, respectively, was recovered. However, in Campaign 3 the amount recovered was 28.7 g. Significantly, in Campaign 3 the PuF_4 fluorination time had been reduced from 5 hr per run (Campaigns 1 and 2) to only 3 hr per run. Thus more plutonium was probably in the bed at the end of Campaign 3 when filter cleanup was started.

Most of the plutonium recovered from the filter region probably reached there by elutriation although thermal decomposition could occur theoretically. The PuF_6 in the gas leaving the bed is cooled in the heat-exchange zone just below the filters. Although the gas is saturated with PuF_6 at the high temperatures (as in the bed or heated disengaging zone),

this situation is not true in the cooling zone just below the filters; i.e., the F_2 - PuF_6 equilibrium is no longer satisfied. Since cooling occurs quickly, decomposition should be kept to a minimum. A kinetic model proposed by Trevorrow and Steindler⁵ predicts that little PuF_6 should decompose.

Of interest also in the filter-cleanup step is that the percentage of the plutonium charge collected in these campaigns is smaller than in earlier runs² in which smaller quantities of plutonium were fluorinated and in which up to 10% of this smaller charge was recovered from the filter region. The current data suggest that the quantity of plutonium remaining in the filter region may be about the same for a wide range of plutonium-charge sizes.

The neutron level in the equipment area, indicative of the quantity of plutonium present, was approximately the same before and after the campaigns, indicating that most of the plutonium that was deposited in the equipment was recovered. One cleanup fluorination to recover these deposits, instead of three (one at the end of each campaign), would have been sufficient to recover the small quantity of plutonium present.

F. Plutonium Concentration in Alumina Bed during Fluorination Period: Comparison of Grab Samples and PuF_6 Collection Data

Data from previous experiments² in which grab samples were removed from two levels of the fluidized bed during a fluorination run showed that the samples were not representative of the bed plutonium composition. In the present campaign-type experiments, the same conclusion was reached by a different method. The quantity of PuF_6 produced in a given time interval was measured by sorbing the PuF_6 directly on NaF, which was later analyzed for plutonium content. Since the amount of plutonium produced in a given time and the quantity of plutonium added to the bed at the start of the run were known, the concentration of plutonium in the bed at the two times could be calculated. An assumption must be made that all the plutonium was in the bed and not on the filter or wall surfaces. The calculated plutonium analyses from PuF_6 production data were plotted on the same graph (Fig. 5) as the plutonium concentrations obtained from analyses of samples removed from the bed. The discrepancy is apparent and reveals the difficulty of obtaining a representative sample of the bed. Tests made earlier² with 48-100 mesh alumina and -325 mesh nickel fines as a stand-in for PuF_4 powder also showed this difficulty.

G. Cold-trap Effectiveness in Collecting PuF_6 from the Recycle-gas Stream

During the PuF_4 fluorination step, fluidizing gas is recycled through the fluorinator and the cold traps. Added to this stream are fluorine for maintaining a high fluorine concentration in the recycle-gas stream and nitrogen for blowback of the filters and purging of the pressure taps.

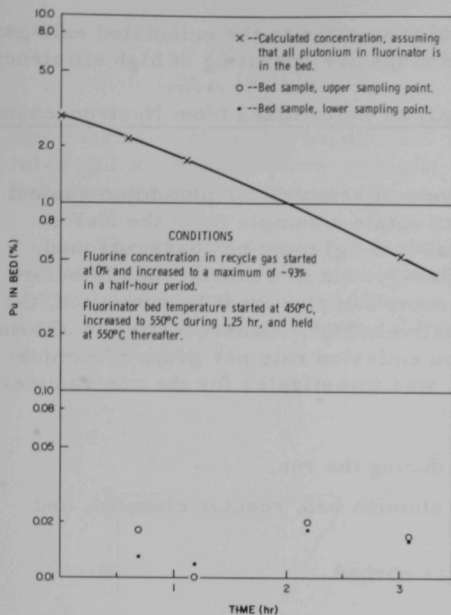


Fig. 5. Comparison of Calculated Plutonium Concentration in Alumina Bed and Plutonium Concentration in Samples Removed from Fluidized Bed, Run 1, Campaign 3

1.2% of the charged plutonium was collected in the NaF-filled trap in the process off-gas line. Thus about 98.7% of the available PuF_6 was collected in the cold traps.

Another way of examining the effectiveness of the cold traps is to compare the coolant temperature with the calculated temperature of the gas leaving the cold trap. The average temperature of the gas leaving the cold traps was calculated by first calculating the average partial pressure of PuF_6 leaving the cold trap (from the NaF sorption data) and then using the PuF_6 vapor-pressure data curve. Vapor-pressure data have not been determined for temperatures below -30°C , and extrapolated data of two investigators were used although this probably introduced some error. If Mandleberg's vapor-pressure data,⁶ determined experimentally in the -29 to 21°C range, are extrapolated, the temperatures of the gas exiting from the cold traps would be -48 , -56 , and -50°C for the three campaigns. If Weinstock's data⁷ for the 0 to 52°C range are extrapolated, the exit-gas temperatures in the three campaigns would be -52 , -61 , and -54°C , which is lower than that obtained by extrapolation of Mandleberg's data. The measured temperature of the coolant circulating through the

A volume of gas about equivalent to the volume of gases added is bled off from the recycle loop; since only a small amount of the fluorine is reacted per pass through the fluorinator, the bleed is at a point downstream from the cold traps. Any plutonium in this off-gas stream is sorbed on NaF. The sorbed plutonium, in a commercial plant, would have to be reprocessed to PuF_6 ; therefore this quantity should be kept as low as possible. The plutonium collected from the process off-gas does not represent a process loss since sorbents, such as LiF instead of NaF, could be used from which the PuF_6 could be desorbed.

The data in Table III show that the two in-series cold traps were effective in collecting the PuF_6 from the recycle-gas stream during the PuF_4 fluorination step. Approximately 92.1% ($90.7 \pm 1.4\%$) of the charged plutonium was collected in the cold traps, while

cold traps is approximately -65°C , which is close to the calculated exit-gas temperatures, indicating that the cold traps are operating at high efficiency.

H. Plutonium Content of NaF and Al_2O_3 as Determined from Neutron-count-rate Data

The preparation and wet analysis of samples for plutonium content are time-consuming. For example, to obtain a sample from the NaF on which the PuF_6 is sorbed, the material (1-3 kg) must be coarse-ground, riffled to obtain a 10-g sample, and fine-ground in a mortar-pestle before being submitted for wet analysis. If many samples must be submitted, the preparation and analytical cost is relatively high. Consequently, an alternative method, which relates the neutron emission rate per gram of sample with plutonium content of the sample, was investigated for the run samples that fall into the following categories:

1. Fluid-bed samples taken during the run.
2. Final samples, including alumina bed, reactor cleanout, and filter-scrappings samples.
3. NaF on which the PuF_6 was sorbed.

All materials were counted in the water-moderated neutron detector. Counter settings, background counting method, equipment setup, and sample placement remained constant for all analyses. A sample was used as a standard to check the consistency of the count rate.

No special sample preparation (e.g., grinding, mixing, or splitting) took place prior to neutron counting. The material was removed from the process units, placed in suitably sized containers, removed from the glove-box in pouches, and counted in the neutron detector. Sample weights and the net neutron counts per minute were recorded. The samples were then prepared and submitted for wet analyses.

The detector used in this program is subject to dead-time count masking at higher count rates. To obtain a real count rate, the following formula was used:

$$R_2 = \frac{R_1}{1 - \text{TR}_1},$$

where

R_1 = observed rate, net counts/min,

R_2 = corrected rate, counts/min,

and

$$T = 1.21 \times 10^{-7} \text{ min.}$$

Since the correction was significant only for material with net count rates of 1×10^5 counts/min or more, only the high-plutonium-content NaF samples were subject to the correction factor.

The neutron count rate in counts/(min)(g) has been plotted as a function of the chemically analyzed plutonium concentration in (a) samples of the fluid bed and final bed (Fig. 6), (b) reactor-cleanout and filter-scraping samples (Fig. 7), and (c) NaF samples on which the product PuF_6 was sorbed (Fig. 8).

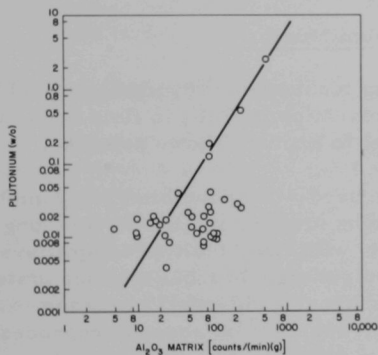


Fig. 6. Neutron Count Rate vs Plutonium Concentration in Samples of the Fluid Bed and Dumped Bed

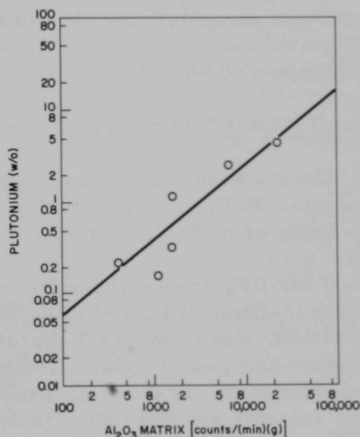


Fig. 7. Neutron Count Rate vs Plutonium Concentration in Reactor-cleanout and Filter-scraping Samples

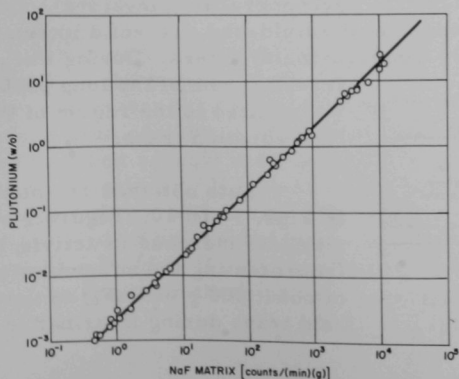


Fig. 8

Neutron Count Rate vs Plutonium Concentration in NaF Sorber Samples

Fluid-bed and final bed samples containing less than 5 w/o plutonium showed little correlation of the two types of analysis. At higher plutonium concentrations, a good correlation may develop, but more data are required before this can be established. The plot for the reactor-cleanout and filter-scraping samples shows that there is some correlation; most of the scatter is in the low-plutonium-concentration region. The scatter noted in the low-plutonium-concentration regions may be due to different americium contents of the samples. Since the fluoride of americium is not volatile, americium builds up in the fluorinator as the campaign proceeds. As the plutonium is fluorinated from the reactor, the ratio of americium to plutonium increases. Because of the scatter, the curve is not usable for accurately determining the plutonium content of these types of samples.

The data obtained for NaF samples (NaF was used to sorb plutonium from the gas streams) provided sufficiently precise estimates of plutonium concentration for most tests. The data cover a wide range of plutonium concentrations, 0.001-26 w/o.

I. Use of Neutron Detectors as Plutonium Monitors

Development of neutron-counting techniques for monitoring (1) the movement of PuF_4 and PuF_6 during fluorination of PuF_4 in fluid beds, and (2) the transfer of PuF_6 from one vessel to another shows promise.

Four BF_3 probe-type units were used--two portable PNC-1 meters (Eberline Instrument Co.) with $2\frac{1}{2}$ -in.-long probes, and two $9\frac{1}{2}$ -in.-long BF_3 tubes (N. Wood Counter Laboratory) with ANL-built preamplifiers and independent power supplies. The output signals from the four units were continuously recorded on a multichannel strip-chart recorder. Similar systems are described in other reports^{8,9} on aqueous reprocessing of plutonium materials (α, n reaction with oxygen).

During the first campaign, the smaller probes were positioned directly in gloves at gloveports adjacent to the two in-series PuF_6 cold traps. The long probes were attached to personnel lifts (elevators). During fluorination, one long probe was opposite the fluid-bed gas-solid interface, the other was opposite the primary sintered-metal filters. During PuF_6

transfer, one of the long probes was shifted to the region of the NaF sorption traps.

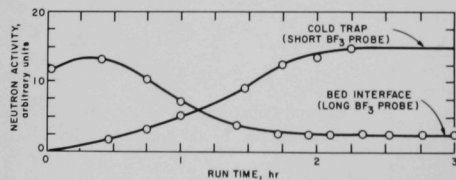


Fig. 9. Neutron-activity Level at Cold Trap and Fluorinator during Fluorination of PuF_4

Data obtained are plotted in Figs. 9 and 10. Figure 9 shows a typical increase in activity (representing the accumulation of about 200 g of PuF_6) in the cold traps during fluorination

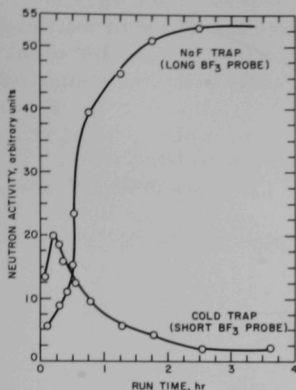


Fig. 10. Neutron-activity Level at Cold Trap and NaF-filled Collection Trap during Transfer of PuF_6

and also a net reduction in the plutonium level in the fluid bed. Fluorination appears to have been complete in about $2\frac{1}{2}$ hr. The shape of the PuF_6 collection curve is similar to that obtained from preliminary weight data in a subsequent campaign.

Typical data obtained during the vapor transfer of PuF_6 from the cold traps to the NaF sorption trap are shown in Fig. 10. Transfer was carried out by heating the cold trap to $\sim 70^\circ\text{C}$ and passing nitrogen through it as a carrier gas. The time when neutron activity at the cold trap decreased corresponded rather well to the time when the activity level at the NaF trap increased. The bulk of the transfer apparently was complete in 1 hr, but because the neutron count rate showed a continued rise, transfer was continued for an additional 2 hr.

J. Metal-corrosion Rate in Fluorinator

Corrosion of the fluorinator metal presents no problems if operating conditions similar to those employed in these campaigns are used. The starting fluorination temperature in each of the three runs of this campaign was 300°C , and $\sim 85\%$ fluorine in nitrogen was used. This was increased in 25°C increments every 15 min until 550°C was reached; this temperature was held for the remainder of the run. Total fluorination time on each campaign was $18\frac{1}{2}$ hr, of which about 10 hr was at 550°C .

A corrosion rate of 10 mils/yr (for 365 days of continuous operation) was calculated from the increase in nickel concentration in the alumina bed during the three runs of a campaign. This may be compared with the 12-40-mils/yr rate found by Chilenskias and Gunderson¹⁰ for metal in contact with a fluidized alumina bed.

Figure 11 is a plot (against time) of the nickel content of the samples taken from the dumped bed at intervals throughout the campaign. The rate of corrosion was 0.22 g/hr. If it is assumed that the nickel came from a surface area consisting of walls of the fluorinator plus the nickel balls used as a bed support medium and gas distributor in the fluorinator, the rate is 10 mils/yr. If it is assumed that the nickel came from the walls only (probably a better assumption since some of the nickel balls of the gas distributor are cooled by the incoming gas), the corrosion rate is about 28 mils/yr. If downtime is considered, the expected corrosion rate would be less than these values.

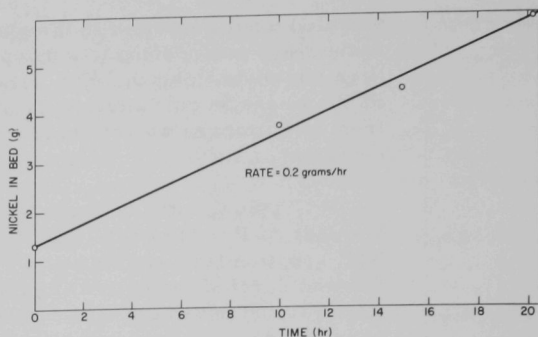


Fig. 11. Amount of Nickel in Bed vs Fluorination Time

K. Efficiency of NaF for Sorption of PuF_6

Data in Table VII confirm information obtained in prior experiments that NaF is an efficient trapping medium for PuF_6 . Gas velocities ranged from 0.07 to 0.7 ft/sec, and superficial contact times (based on free cross-sectional area) from 3.7 to 63.4 sec. In the transfer of PuF_6 from the first cold trap, a loading of 25.6% plutonium (346 g of plutonium sorbed on 885 g of NaF) was achieved. Maximum loading, assuming that the compound $3\text{NaF} \cdot \text{PuF}_4$ was formed, would have been 63% plutonium.

TABLE VII. Plutonium Concentrations in Sections of NaF-filled Traps Used for Sorption of PuF_6

Trap No.	Section No.	Process Step	NaF Charged to Section (g)	Pu in Sample from Section (%)	Gas Velocity in Trap (ft/sec)	Contact Time in Trap (sec)
1	1	Transfer from first cold trap	885	25.6	0.07	63.4
	2		885	18.4		
	3		885	0.5		
	4		885	< 0.1		
	5		885	< 0.1		
	6		885	0.01		
2	1	Transfer from second cold trap	530	1.3	0.07	31.7
	2		530	0.1		
	3		530	0.1		
	4	Process off-gas during fluorination of PuF_4	530	0.2	0.13	17.2
	5		530	0.5		
3	1	Collected during cleanup of fluorination filters	530	0.7	0.60	3.7
	2		530	< 0.1		
	3		530	< 0.1		
	4	Collected during cleanup of cold traps	530	< 0.1	0.60	3.7
	5		530	1.3		

To minimize the number of traps handled in each run but still collect the necessary information, some of the traps were used in two applications. For example, Trap 2 was used initially to remove PuF_6 from the process off-gas during the fluorination and PuF_4 , and later to collect PuF_6 transferred out of the second cold trap. To separate the quantities of PuF_6 , the

gas flow initially was upward through the trap and later downward. The data in Table VII show that the plutonium amounts from the two process steps could be separated, very little plutonium being found on the middle layers of the traps.

Only the data from the second campaign have been included, but those from the first and third campaigns show similar good sorption efficiency.

L. Concentration of Americium in Fluorinator Alumina Bed

Americium content was significant in the bed because of the decay of the relatively high ^{241}Pu (458-yr half-life) content of the PuF_4 (~2.4%). The americium does not volatilize during the fluorination step and can be expected to build up in the bed of the fluorinator. The americium concentration (data from X-ray spectrographic analysis based on calibrations with plutonium) of the bed after the first, second, and third fluorination runs was expected to increase in a 1, 2, 3 ratio since the same charge was added in each fluorination run. Data actually show a 1, 1.4, 1.8 ratio (0.005, 0.007, and 0.009% americium) in bed samples from the successive fluorination runs. This suggests that the bed samples may not be representative of the bed contents, or that analysis is not accurate at these low concentrations, or that americium collected selectively on the filter. Further data are needed. Detection of americium in the plutonium product or the secondary-filter chamber may also provide a measure of the efficiency of the sintered-metal filters in passing submicron-size particles.

V. CONCLUSIONS

The results of the present series of campaign-type experiments, which involved the fluorination of almost 2.3 kg of PuF_4 to PuF_6 with elemental fluorine, have shown that good production rates at high fluorine efficiencies and satisfactory plutonium material balances can be achieved. Plutonium deposited in equipment by radiation and thermal-decomposition mechanisms, by elutriation from the fluidized bed, and as a result of reaction with minor chemical constituents or metal surfaces can be recovered by refluorination at 300°C.

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